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(54) **Halocarbon-free solvent cleaning method**

(57) An article, such as a PCB after soldering, is cleaned by contacting it with the vapour phase of an azeotropic, substantially halocarbon-free mixture of an alcohol with an alkane and/or cycloalkane. The article may be pre-immersed in the azeotropic mixture and/or may be treated with an alkyl ester of a carboxylic acid, before it is contacted with the said vapour phase.

The invention avoids the use of toxic halocarbon solvents.

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Solvent Cleaning Method

The present invention relates to the cleaning of articles, and more especially to methods of cleaning articles using solvents. The method of the invention is of particular advantage in the defluxing of, for example, printed circuit boards (PCBs), after soldering.

In many previously known methods for solvent cleaning of articles, for example, PCBs, solvent mixtures that are azeotropic or that exhibit azeotrope-like behaviour have been used as the cleaning substance (see for example European Patent Specifications Nos. 0183109, 0183110, 0334384, British Patent Specification No. 2226570 and U.S. Patent Specifications Nos. 4654160, 4655956 and 4816175). Those solvent mixtures contain as a major component a halocarbon. For example, British Specification No. 2226570 discloses a composition having azeotropic properties and containing, by weight, 61.7 to 70.0% 1,1,2-trichloro-1,2,2-trifluoroethane, 5.1 to 6.5% methanol, 0.05 to 0.6% nitromethane, 21.0 to 30.0% 1,2-dichloroethylene, 0.3 to 1.0% acetone and 0.5 to 5.0% hexane.

It has become recognised in recent years that halocarbon solvents have a particularly harmful effect on the environment. Further, because of their toxicity, special precautions are required in the storage, handling and disposal of the mixtures. It is therefore desirable to avoid the use of halocarbon solvents, if possible.

European Patent Specification No. 0104633A discloses a method of cleaning work-pieces in which the work-pieces are immersed in a first bath containing an azeotropic solvent mixture and are subsequently suspended above a
5 second bath that communicates with the first bath, and sprayed with further solvent mixture. The azeotropic mixture in the first and second baths may consist of, for example, hexane and isopropyl alcohol.

There remains scope for improvement in the
10 effectiveness of the previously known processes.

The invention provides a method of cleaning an article, comprising contacting the article with the vapour phase of an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cyclo-
15 alkane.

Advantageously, the article is immersed in an alkyl ester of a carboxylic acid, said ester being at a temperature of 90°C or less, before it is contacted with the said vapour phase. The ester may be used alone or in
20 combination with another organic liquid, for example, an alcohol or hydrocarbon. In addition to, or instead of, immersing the article in the ester, the article may be immersed in an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or a cycloalkane
25 before it is contacted with the said vapour phase. If the article is immersed both in the ester and in the azeotropic mixture, it is preferably immersed first in the ester and subsequently in the azeotropic mixture.

After it has been contacted with the vapour phase, the article will normally be dried, for example, in air.

In another aspect, the present invention provides a method of cleaning an article, comprising the steps of

5 (i) immersing the article in an alkyl ester of a carboxylic acid, the said ester being at a temperature of 90°C or less; and

 (ii) treating the article with an azeotropic, substantially halocarbon-free mixture of an alcohol with
10 an alkane and/or cycloalkane.

 The article may in step (ii) be immersed in an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cycloalkane. Instead, or in addition, the article may in step (ii) be contacted
15 with the vapour phase of an azeotropic, substantially halocarbon-free mixture of an alcohol with an alkane and/or a cycloalkane.

 The invention also provides a method of cleaning a article, comprising immersing the article in an azeo-
20 tropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or a cycloalkane, the mixture being substantially isolated from any liquid to be used in any treatment of the article prior or subsequent to its immersion in the mixture.

25 The substantially halocarbon free azeotropic mixtures used in accordance with the invention advantageously contain not more than 1000ppm halogen-containing compound.

In those processes in which the article is immersed in a first azeotropic mixture, and then suspended in the vapour phase of a second azeotropic mixture, the components of the first and second azeotropic mixtures are advantageously the same.

In those cases in which an article is first immersed in one azeotropic mixture and then suspended in the vapour phase of an identical azeotropic mixture, the immersion may be performed in a first batch of the azeotropic mixture and the article may then be suspended in the vapour phase generated by a second batch of liquid. The two batches of liquid are preferably isolated from one another in that, with the exception of any residual liquid carried on the article, there is no transfer of components in the liquid phase from one batch to the other.

The expression "azeotropic mixture" is used herein to refer to solvent mixtures composed of two or more components, the composition of which, on boiling or evaporation of the liquid, remains substantially unchanged.

As the alkyl ester of a carboxylic acid there may be used C_1 to C_{12} -alkyl esters of alkane monocarboxylic acids that contain from 1 to 6 carbon atoms in the acid moiety. The alkyl group may be straight-chain or branched. The alkyl group may be, for example, one having from 5 to 16 carbon atoms. Especially suitable as alkyl groups are alkyl groups with from 6 to 13 carbon

atoms, for example, isohexyl, isoheptyl, isooctyl, isononyl, isodecyl and isotridecyl. The ester is preferably an acetate, for example, isohexyl acetate, isoheptyl acetate, isooctyl acetate, isononyl acetate, isodecyl acetate, isotridecyl acetate. The alkyl ester may especially advantageously be isodecyl acetate. The use of the prefix "iso" herein in relation to the alkyl radicals of the ester denotes mixtures of alkyl radicals that have the same carbon number but differ from one another in the degree of branching, at least a major proportion of the alkyl radicals being branched chain, and advantageously at least 85% being branched chain. The carbon atom linked to the oxygen atom of the acid moiety is advantageously unsubstituted in substantially all, that is, at least 95%, of the alkyl radicals. For example, the term "isodecyl" is used herein in relation to compounds to refer to mixtures of decyl compounds that differ from one another in the structure of the decyl group, at least a major proportion of the decyl radicals being branched chain, and advantageously at least 85%, preferably 90%, being branched chain. Advantageously, the carbon atom linked to the oxygen of the acid moiety is unsubstituted in substantially all, i.e., at least 95%, of the decyl radicals. Advantageously, also, the α -carbon atom is substituted in at least 15% of radicals. Advantageously, a major proportion, preferably at least 75%, of the decyl radicals are dimethyl octyl radicals,

for example, the radicals are 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 4,6-, and 4,7-dimethyl radicals.

The carboxylic acid alkyl ester may optionally be in admixture with another organic liquid, for example, an alcohol or a hydrocarbon. As alcohol there may be used, for example, an aliphatic alkyl alcohol having a single hydroxy group and from 5 to 16 carbon atoms, in which the carbon chain is straight or branched. The alcohol may advantageously be the alcohol from which the alkyl group of the ester is derived. As hydrocarbon there may be used, for example, a saturated aliphatic or cyclic hydrocarbon having from 6 to 13 carbon atoms. Preferably, the hydrocarbon will have a flash point that is of the same order as that of the ester. More than one alcohol and/or more than one hydrocarbon may be present. The amount and nature of the alcohol and/or hydrocarbon solvents present will be selected so as to optimise the solvency properties of the formulation having regard to the nature and amount of dirt present on the article to be cleaned, the selection, having regard to the articles to be cleaned, of appropriate solvents and their proportions being a routine matter for those skilled in the art.

In the azeotropic, substantially halocarbon-free, mixtures of an alkane and/or cycloalkane with an alcohol there may be used as alkane a straight or branched chain alkane having from 5 to 10, and preferably from 6 to 8, carbon atoms. As cycloalkane, there may be used a

cycloalkane having from 4 to 7 carbon atoms in the ring and having a total of from 5 to 10 carbon atoms. The mixture may, if desired, contain an alkane and a cycloalkane. As cycloalkane there may advantageously be used a C₆ to C₈ cycloalkane, that preferably has a 6-membered ring. The alcohol may be an aliphatic alkyl alcohol having a single hydroxy group and from 1 to 6 carbon atoms, preferably 3 to 5 carbon atoms, in which the carbon chain is straight or branched. For example, there may be used as azeotropic mixtures mixtures of sec-butyl alcohol with isooctane, or mixtures of isopropyl alcohol with one or more of the following: n-heptane, isoheptane and methylcyclohexane. (The prefix "iso" is used herein in relation to isoheptane and isooctane in the sense in which it is used above in relation to the isoalkyl groups of ester compounds.) Advantageously, a mixture of heptane isomers comprising n-heptane, isoheptane and methylcyclohexane, is used as one of the components of the azeotropic mixture, the alcohol component then being, for example, isopropyl alcohol; the azeotropic mixture may in that case have a boiling temperature range of, for example, 2°C.

The mixture may, for example, be a mixture of, by weight, 47% methylcyclohexane and 53% isopropyl alcohol, which mixture has a boiling temperature of 77°C at atmospheric pressure.

If the article is to be immersed in an azeotropic mixture, that mixture is preferably contained in an

ultrasonic bath, the article being subjected to sonication in the said bath. Sonication has been widely used in previously known solvent cleaning methods and the selection of suitable sonication conditions will be a routine matter for the person skilled in the art. The article may be immersed in an azeotropic mixture without sonication before it is contacted with the vapour phase of the same, or another azeotropic mixture. It will then be advantageous for the article to be immersed in the mixture from which the said vapour phase is generated, as only one treatment vessel is then necessary for both those treatment steps.

In those processes in which the article is immersed in a carboxylic acid alkyl ester or a mixture of a said ester with another organic liquid, the article is preferably immersed in an ultrasonic bath containing the ester or ester-containing mixture, and sonicated.

The temperature of the ester or ester-containing mixture is preferably not greater than 90°C.

The ester or the ester-containing mixture is preferably at a temperature of greater than 50°C, for example, at approximately 70°C.

Certain illustrative embodiments of the invention will now be described, by way of example.

Example 1a

After soldering of electronic components, a PCB is immersed in an ultrasonic bath containing an azeotropic

mixture of, by weight, 47% methylcyclohexane and 53% isopropyl alcohol. The mixture is sonicated at equilibrium temperature (that is, the temperature at which losses of energy from the ultrasonic bath by, for example, evaporation of mixture and transfer of heat to articles being dipped are equal to the input of energy by sonication) for a period of 90 seconds. The PCB is removed from the ultrasonic bath, allowed to cool for 60 seconds, and is then suspended for 90 seconds in the vapour phase that is formed by boiling a mixture of, by weight, 47% methylcyclohexane and 53% isopropyl alcohol. The vapour phase is enclosed in a chamber in the presence of the boiling azeotropic mixture, with which it is in equilibrium. The upper walls of the chamber are provided with cooling means for condensing, and thereby preventing escape to the atmosphere of the vapour. The effect of the said cooling means on the temperature of the bulk of the vapour is minimal and the temperature of the vapour phase other than in the direct vicinity of the cooling means approximates the boiling temperature of the mixture. The PCB is then removed from the vapour phase and dried in air for 1 minute.

Example 1b

A PCB is cleaned in accordance with the procedure described in Example 1a except that, instead of immersing the PCB in an ultrasonic bath containing the azeotropic mixture and sonicating, the PCB was immersed in an

azeotropic mixture of the same composition, but without any sonication.

Example 2a

5 A PCB is cleaned as described in Example 1 except that, before it is immersed in the ultrasonic bath, the PCB is immersed in isodecyl acetate at a temperature of 70°C, residual ester being removed from the PCB before it is immersed in the azeotropic mixture.

10

Example 2b

 A PCB is cleaned in accordance with the method of Example 2a except that, instead of immersing the PCB in an ultrasonic bath containing the azeotropic mixture and
15 sonicating, the PCB is immersed in an azeotropic mixture of the same composition, but without any sonication.

Example 3a

 After soldering of electronic components, a PCB is
20 immersed in an ultrasonic bath containing isodecyl acetate at 70°C, with sonication, and then removed and allowed to cool for 60 seconds. Residual ester is removed from the PCB. The PCB is then suspended for 30 seconds in the vapour phase that is formed by boiling a
25 mixture of, by weight, 47% methylcyclohexane and 53% isopropyl alcohol, and cooled again for 60 seconds, and those two steps are then repeated twice. The vapour phase is enclosed in a chamber in the presence of the

boiling azeotropic mixture, with which it is in equilibrium. The upper walls of the chamber are provided with cooling means for condensing, and thereby preventing escape to the atmosphere of the vapour. The effect of the said cooling means on the temperature of the bulk of the vapour is minimal and the temperature at the vapour phase other than in the direct vicinity of the cooling means approximates the boiling temperature of the mixture. Cooling of the PCB after contacting with the vapour is accomplished by holding it near to the cooling means. After treatment, the PCB is dried in air for 1 minute.

Example 3b

A PCB is cleaned as described in Example 3a except that, instead of immersing the PCB in an ultrasonic bath containing isodecyl acetate and sonicating, it is immersed in isodecyl acetate without sonication.

Comparative Example A

After soldering of electronic components, a PCB is dipped in an ultrasonic bath containing isopropyl alcohol. Sonication is carried out at equilibrium temperature for 90 seconds. The PCB is cooled for 60 seconds and then suspended for 90 seconds in the isopropyl alcohol vapour phase that is created by boiling isopropyl alcohol in a second bath. The PCB is then dried in air for 1 minute.

Comparative Example B

A PCB is cleaned in accordance with the procedure described in Comparative Example A except that, instead of immersing the PCB in an ultrasonic bath containing isopropyl alcohol and sonicating, the PCB is immersed in isopropyl alcohol without sonication.

A number of PCBs were cleaned by each of the procedures of Examples 1 to 3 and Comparative Examples A & B and the cleaned PCBs were inspected and the quality of cleaning assessed. The results are given in the Table:

S A M P L E				
CLEANING PROCEDURE	ULTRASONICS APPLIED			NO ULTRASONICS
	I	II	III	IV
Comparative Example A	B	A	A	-
Comparative Example B	-	-	-	B
1a	C, D	E, E, D	E, C	-
1b	-	-	-	C
2a	D	-	B	-
2b	-	-	-	D
3	D	-	-	D

A : poor

B : below average

C : acceptable

D : good

E : very good

As may be seen from the Table, the cleaning results obtained in Examples 1 to 3 are significantly better than those obtained in Comparative Examples A and B.

Effective cleaning is obtained both with and without an ester pretreatment step.

While the invention has been described above in relation to the cleaning of printed circuit boards after soldering, it will be appreciated that the invention may be used in other applications in which solvent cleaning is suitable. For example, the invention provides an effective means of degreasing solid surfaces, for example, of metal articles having intricate parts.

Claims

1. A method of cleaning an article, comprising contacting the article with the vapour phase of an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cycloalkane.
2. A method according to claim 1, in which the article is immersed in an alkyl ester of a carboxylic acid before it is contacted with the said vapour phase.
3. A method according to claim 1 or claim 2, in which the article is immersed in an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cycloalkane before it is contacted with the said vapour phase.
4. A method according to any one of claims 1 to 3, in which the temperature of the vapour phase with which the article is contacted is substantially the boiling temperature of the azeotropic mixture.
5. A method of cleaning an article, comprising the steps of
 - (i) immersing the article in an alkyl ester of a carboxylic acid; and
 - (ii) treating the article with an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or a cycloalkane.
6. A method according to claim 5, in which, in step (ii), the article is immersed in an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cycloalkane.

7. A method according to claim 5 or claim 6, in which, in step (ii), the article is contacted with the vapour phase of an azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or a cyclo-
5 alkane.

8. A method according to claim 5, in which, in step (ii), the article is immersed in a first azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or a cycloalkane and is then contacted with
10 the vapour phase of a second azeotropic, substantially halocarbon-free, mixture of an alcohol with an alkane and/or cycloalkane.

9. A method according to claim 3 or claim 8, in which the vapour phase is of substantially the same composition
15 as the azeotropic mixture in which the article is immersed.

10. A method according to any one of claims 1 to 4 and 7 to 9, in which the vapour phase is generated by boiling an azeotropic mixture of isopropyl alcohol with one or
20 more C7 alkanes selected from n-heptane, isoheptane and methylcyclohexane.

11. A method according to claim 10 in which the vapour phase is generated by boiling an azeotropic mixture of methylcyclohexane and isopropyl alcohol.

12. A method according to any of claims 2, 3, 6 and 8, in which the azeotropic mixture in which the article is
25 immersed is substantially isolated from the azeotropic

mixture from which the vapour phase with which the article is to be contacted is generated.

13. A method of cleaning an article, comprising immersing the article in a first azeotropic, halocarbon-free, mixture of an alcohol with an alkane and/or a cycloalkane and contacting the article with the vapour phase of a second azeotropic, halocarbon-free mixture of an alcohol with an alkane and/or a cycloalkane, the first mixture being substantially isolated from the mixture from which the said vapour phase is generated.

14. A method of cleaning an article, substantially as described herein.

15. An article that has been cleaned by a method according to any of claims 1 to 14.

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Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK CI (Edition K) C5D DAA

(ii) Int CL (Edition 5) C11D

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MR R STAGG

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: EDOC, WPI

Date of Search

23 APRIL 1992

Documents considered relevant following a search in respect of claims

1-15

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP A 0104633 (HONEYWELL INC) See pages 7-8 and Claims 1, 2, 4 and 10	5, 6, 9
Y	DE A 2732148 (SIEMENS)	1, 5

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

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